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GRANT or CONTRACT: N00014-91J-0201

R&T CODE: 4133032

Robert J. Nowak

TECHNICAL REPORT NO. 53

by G. L. Hornyak, C. J. Patrissi, C. R. Martin, J-C Valmalette, L. Lemaire, J.
Dutta and H. Hofmann

Prepared for Publication

in

Nanostructured Materials

Colorado State University
Department of Chemistry
Fort Collins, CO 80523-1872

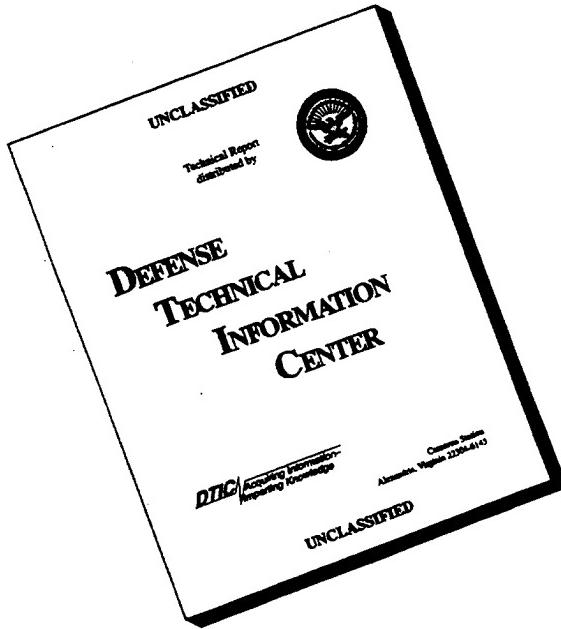
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2. September 30, 1996

3. Interim report

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13. Abstract: The optical constants n_{Al} and k_{Al} of a 50/50 volume fraction Au/Ag alloy were derived synthetically by application of a Bruggeman (BG) effective medium expression. The alloy data base was then input into a Maxwell-Garnett (MG) effective medium expression to determine the absorption maximum of the nano-alloy/insulator composite (the volume fraction of the nano-alloy was equal to 5%). The absorption maximum (λ_{max}) of the hypothetical composite was found to be 499 nm for spherical particles and was blue-shifted relative to that of a composite containing pure gold nanospheres (499 vs. 528 nm respectively). The transmission color at this wavelength was a red-orange. λ_{max} in the range 512 to 519 nm (Au/Ag alloy between 60/40 - 70/30 volume fraction respectively) is needed to obtain the scarlet-red exhibited by the famous Lycurgus cup of 4th century Rome.

14. Subject terms: Nanomaterials, nanometals, optical properties

17. 18. 19. Unclassified

EFFECTIVE MEDIUM THEORY CHARACTERIZATION OF Au/Ag NANOALLOY-POROUS ALUMINA COMPOSITES

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Abstract - The optical constants n_{Al} and k_{Al} of a 50/50 volume fraction Au/Ag alloy were derived synthetically by application of a Bruggeman (BG) effective medium expression. The alloy data base was then input into a Maxwell-Garnett (MG) effective medium expression to determine the absorption maximum of the nano-alloy/insulator composite (the volume fraction of the nano-alloy was equal to 5%). The absorption maximum (λ_{max}) of the hypothetical composite was found to be 499 nm for spherical particles and was blue-shifted relative to that of a composite containing pure gold nanospheres (499 vs. 528 nm respectively). The transmission color at this wavelength was a red-orange. λ_{max} in the range 512 to 519 nm (Au/Ag alloy between 60/40 - 70/30 volume fraction respectively) is needed to obtain the scarlet-red exhibited by the famous Lycurgus cup of 4th century Rome (1).

INTRODUCTION

The lower limit of the absorption maximum for infinitely small spherical nano-gold metal particles which form the minor component of a composite embedded in an insulating medium of refractive index equal to 1.6 is ca. 528 nm (that of pure infinitely small spherical Ag is near 410 nm). The color of such a composite is ruby red when viewed upon transmission, and therefore, the scarlet red found in the Lycurgus cup is not possible with pure gold inclusion. By fabricating particles that are of higher aspect ratio and oriented perpendicular to the electric field of the incident radiation, this lower limit can be bypassed and scarlet red can be seen. However, orienting particles in this fashion for colored glasses is not practical as spherical particles are naturally formed during the thermal reduction-agglomeration process. A better means is to alloy the Au with Ag. The optical constants for the alloy should lie somewhere in between those of the pure materials. A blue shift in λ_{max} is then possible without having to change the shape of the nanoparticle.

In this paper, we present a means of deriving the optical constants theoretically and applying them to simulate λ_{max} for a composite which contains the Au/Ag alloy. An effective medium expression derived by Bruggeman (2) is used. BG is appropriate when the volume fractions of the components are of similar magnitude. This is the case for an alloy which is ~50/50 by volume. Its form is given below.

$$0 = f_{Au} \left(\frac{\tilde{\epsilon}_{Au} - \tilde{\epsilon}_{Al}}{\tilde{\epsilon}_{Au} + 2\tilde{\epsilon}_{Al}} \right) + f_{Ag} \left(\frac{\tilde{\epsilon}_{Ag} - \tilde{\epsilon}_{Al}}{\tilde{\epsilon}_{Ag} + 2\tilde{\epsilon}_{Al}} \right)$$

$\tilde{\epsilon}_{Al}$, $\tilde{\epsilon}_{Au}$ and $\tilde{\epsilon}_{Ag}$ are the complex dielectric functions of the alloy, the pure Au and the pure Ag respectively. f_{Au} and f_{Ag} (equal to 50% each) are the magnitudes of the volume fractions of the gold and silver. The 2 indicates that the particles are spherical. The equation is solved for $\tilde{\epsilon}_{Al}$ from which the optical constants n_{Al} and k_{Al} , the refractive index and absorption coefficient of the alloy respectively, are extracted.

The wavelength dependent optical constants of the alloy just formed are then input into the MG expression (3). The fundamental assumptions of MG require that the particles conform to the quasistatic requirement (particle size significantly smaller than the wavelength of the analytical beam: $r \ll 0.1 \lambda$) and that the volume fraction of the metal be significantly smaller than that of the host: $f_{Al} \ll f_0$. These conditions are similar to those found in a colored glass. The MG expression is shown below.

$$\frac{\tilde{\epsilon}_c - \tilde{\epsilon}_o}{\tilde{\epsilon}_c + 2\tilde{\epsilon}_o} = f_{Al} \left(\frac{\tilde{\epsilon}_{Al} - \tilde{\epsilon}_o}{\tilde{\epsilon}_{Al} + 2\tilde{\epsilon}_o} \right)$$

$\tilde{\epsilon}_c$ is the dielectric function of the composite and $\tilde{\epsilon}_o$ is the dielectric function of the insulating host material, alumina in this case. f_{Al} is the volume fraction of the alloy in the composite.

Rigid band models assume that the optical properties (i.e. dependent on Fermi energies, etc.) for a binary material behave in a linear fashion with respect to the parent materials. In other words, the optical properties of an alloy are some weighted average of those of the parent materials. We explore this from a phenomenological point of view by means of effective medium theories and compare spectra based on the rigid (average) model and those found by BG and MG.

RESULTS and DISCUSSION

The wavelength dependent optical constants of the alloy n_{Al} and k_{Al} determined by BG and by averaging are shown in Figure 1 along with those of the pure components. It can be seen that both respective simulated curves lie in between those of the two pure components but cannot be considered as identical. After application of the MG expression, the calculated spectra of the nano-alloy/insulator was determined for both the BG and the average optical constant data bases. The results are shown in Figure 2. The position of maximum absorption, λ_{max} , of the BG-alloy composite was determined to be 499 nm. There was no clear absorption maximum in the MG generated spectrum using the average-alloy optical constant data base. In the longer wavelength pure Drude region for gold above 499 nm, the BG- and average-alloy absorption spectra are nearly identical. A 3rd and 4th spectra consisting of binary alloys of 60/40 and 70/30 volume proportion are also shown in Figure 2. The deep scarlet red found in the Lycrus cup lies somewhere between λ_{max} of 512 and 519 nm respectively of the two alloy compositions.

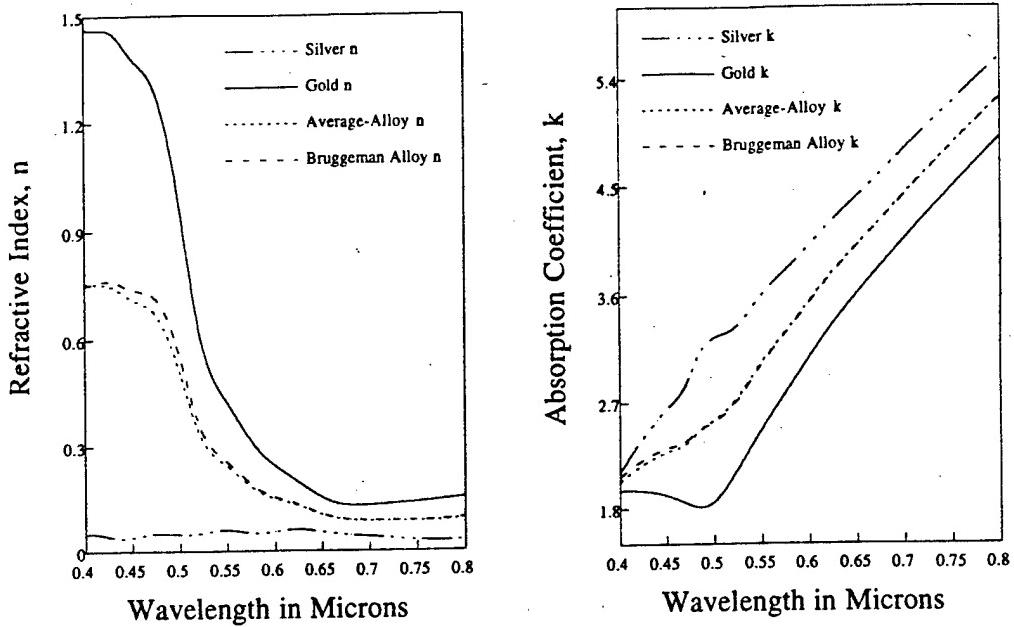


Figure 1. The alloy n_{Al} (left) and k_{Al} (right) calculated by BG are shown between the curves representing the pure components. Optical constants derived by averaging pure values are also shown and slight differences with BG are apparent.

CONCLUSIONS

We have shown theoretically that the absorption maxima of composites containing spherical inclusions of alloyed Au and Ag nanoparticles should demonstrate λ_{max} that are blue shifted relative to pure gold and red shifted relative to pure silver ($\lambda_{max} = 410$ nm). The optical data bases of the alloyed material was formed from a Bruggeman effective medium theory application with 50/50, 60/40 and 70/30 Au/Ag volume fractions. The spectrum of the composite containing the alloy within an insulating host matrix was accomplished by application of the MG effective medium expression in which $f_{Al} = 5\%$. We predict that a binary alloy composition between 60/40 and 70/30 Au/Ag will produce the desired scarlet red color (512 to 519 nm respectively). It is apparent from the figures that in this case averaging optical properties of parent materials will not produce a legitimate spectrum.

The presence of Au/Ag alloys in the glass of the Lycurgus cup has been verified by analytical means (1). In the future, we shall test experimentally the premises discussed in this paper. The application of the dynamical version of the Maxwell-Garnett formulation (DMG) when alloyed particles with finite size are present in composites will also be accomplished (4).

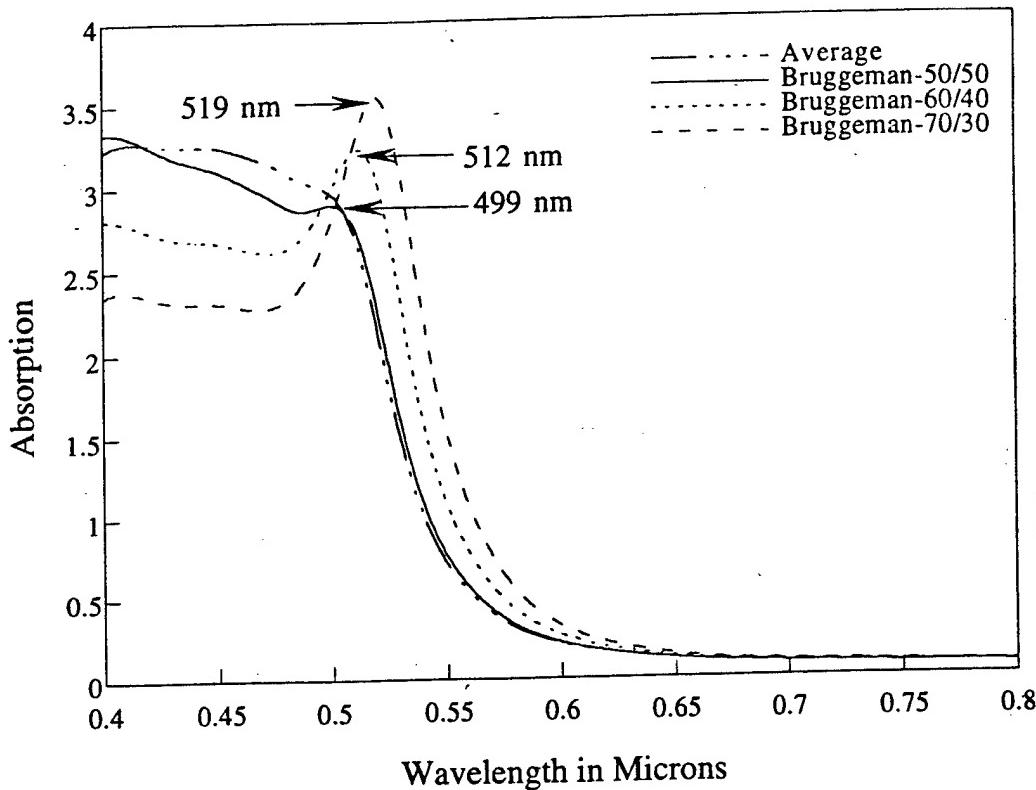


Figure 2. λ_{\max} of the 50/50 Au/Ag alloy composite was 499 nm. That of Au was near 528 nm and that of Ag near 410 nm. The average-alloy composite showed no clear absorption. Two other alloy composites are shown:
70/30 at 519 nm and 60/40 at 512 nm.

ACKNOWLEDGMENTS

We wish to thank the Office of Naval Research (ONR), Grant #: N00014-93-1-0945, for providing funding and special thanks to Professor Colby A. Foss, Jr. of the Department of Chemistry of Georgetown University for developing programs used in this paper.

REFERENCES

1. D.J. Barber and I.C. Freestone, *Archaeometry*, 32, 33, 1990.
2. D.A. Bruggeman, *Ann. Phys. (Leipzig)*, 24, 636, 1935.
3. J.C. Maxwell-Garnett, *Philos. Trans. R. Soc. London*, 203, 385, 1904.
4. C.A. Foss, Jr., G.L. Hornyak, C.R. Martin; *J. Phys. Chem.* 98, 2963, 1994.

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